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COMPLETE SPECIFICATION

NO DRAWINGS

Process for Treating Cellulosic Material and Product Thereof

We, DEERING MILLIKEN RESEARCH CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of P.O. Box 1927, Spartanburg, South Carolina, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of cellulosic materials having improved configurational memory and to the cellulosic materials thus produced.

It is known that cellulosic yarns and fabrics can be produced having good configurational memory in a wet state, e.g. good recovery from wrinkling when the fabric is passed through the spin cycle of an automatic washer and then line dried, by cross linking the cellulosic molecules of the material with a strong base catalyzed cross-linking agent in the presence of moisture so that the reaction occurs while the cellulosic material is hydrated and in the desired configuration. It is, however, characteristic of such a cross-linking reaction that materials thus cross-linked, while having good configurational memory in the wet state, have relatively little or any resistance to or recovery from distortion, e.g. wrinkling, in the dry state under the reaction conditions heretofore employed.

A method of treating cellulosic yarns and fabrics to impart configurational memory in the wet state is described in British Patent Specification No. 855547. Also, methods for imparting dimensional stability to cellulosic fabrics are described in British Patent Specifications Nos. 696282 and 724096. In each of these methods epichlorohydrin or a compound which is connected to epichlorohydrin in the presence of alkali may be used as cross-linking agent.

It has now been found that the above described cross-linking reaction can be modified to provide cellulosic materials having good configurational memory in both the wet and dry states. This means that yarns and fabrics woven or knit from such yarns can be produced which will straighten themselves when crumpled in either the wet or dry state. Also, fabrics treated in the above described manner can be washed in an automatic washer and passed through the spin cycle thereof and thereafter line dried or dried in an automatic tumble dryer and will be obtained in a relatively wrinkle-free state. Also garments produced from such fabrics will resist mussing in the stored state or while worn.

It is therefore an object of this invention to provide a method for producing cellulosic materials having good configurational memory in both the wet and dry states.

It is another object to provide a process for producing cellulosic materials having good configurational memory in both the wet and dry states by only one chemical reaction.

A further object is to provide a method for producing cellulosic materials having both wet and dry configurational memory in an economical and expedient manner.

Still another object is to provide a novel method of producing fabrics having good wet and dry configurational memory so that they can be washed and dried in any manner and obtained in a relatively wrinkle-free state.

Cellulosic materials which are cross-linked according to the process of this invention are those which are normally cross-linked to impart wet configurational memory thereto, e.g., natural and regenerated cellulose including those having a portion of the free

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hydroxy groups esterified, e.g., as a lower-hydrocarbon ester, including the acetate, propionate, butyrate and benzoate, or the inorganic esters such as sulfate, phosphate, and aryl and alkyl sulfate, or etherified, e.g., lower-alkyl, including methyl and ethyl, hydroxyalkyl including hydroxyethyl, carboxymethyl, and the other known cellulose esters and ethers. The natural cellulosic materials can be cotton, linen, jute or flax, and the synthetic cellulosic materials can be in the form of filament or staple viscose rayon, both unmodified and modified, e.g., the polynosic rayons. The novel process is directed primarily and preferably to cellulosic textile fabrics, both knitted, non-woven and woven, but the advantages of this invention can also be achieved by treating the cellulosic yarns or threads employed to produced these fabrics. The preferred cellulosic material is cotton fabric which is preferably woven, e.g., printcloth, broadcloth and sheeting. Although the process will ordinarily be conducted on cellulosic material consisting entirely of cotton or viscose rayon, the process is equally applicable to yarns and fabrics comprising synthetic filaments or fibers, e.g., the glycol-terephthalate polyesters, nylon and the polyacrylic fibers. Preferably the the cellulosic material comprises at least 40% or more by weight of the material to be treated and more desirably 60% or more.

The strong base catalysts for the cross-linking reaction include the alkali-metal hydroxides, e.g., sodium hydroxide and potassium hydroxide, the quaternary ammonium hydroxides, e.g., trimethylphenyl ammonium hydroxide, and alkali-metal salts which, in the presence of moisture, produce a strongly alkaline solution, e.g., the alkali-metal sulfides and alkali-metal silicates. When the salts are employed, they should be employed in amount which will impart an alkalinity to the solution in about the same range as that obtained when an alkali-metal hydroxide is employed. The strong base may be defined as one having a pH of at least 10 as a 1% by weight aqueous solution.

The cross-linking agents employed in the process of this invention are epichlorohydrin and compounds which are converted to epichlorohydrin in the presence of strong bases. 1. 3-dichloropropanol-2, 2, 3-dichloropropanol-1, and mixtures thereof are examples of compounds which are converted to epichlorohydrin in the presence of strong base. Epichlorohydrin is unique among the alkaline catalyzed wet cross-linking agents. Because it consumes only one molar equivalent of alkaline catalyst, the amount of alkaline catalyst which must be applied to the fabric to produce the desired degree of cross-linking is less than that required with other cross-linking agents. Also, its volatility ensures that uniform cross-linking will take place so long as the alkaline catalyst is uniformly distributed on the cellulosic material, even though the epichlorohydrin itself is not absolutely uniformly applied. This uniformity of cross-linking can be most advantageously achieved by maintaining the cellulosic material in a compact package during the cross-linking reaction, e.g., fabric in the form of a smooth roll and yarn in the form of a wound package.

The term "configurational memory" as used herein means that the cellulosic material treated according to the present process tends to return to the configuration in which it was in when the cross-linking reaction took place after being distorted or crumpled. In the case of yarn, this means that the yarns can be compacted and if they were cross-linked in an uncrumpled state, e.g., wound on a package, the yarns will tend to straighten themselves. Fabrics knitted or woven from such treated yarns will also resist wrinkling and mussing. If the yarn is cross-linked in a crumpled position, the resulting yarn and fabric prepared therefrom will have a bulked effect and will resist being distorted into a smooth configuration. When fabrics are treated in a smooth, i.e., wrinkle-free, state the cross-linked fabric will thereafter resist wrinkling. If cellulosic material has only wet configurational memory, it will display good resistance to distortion while in the wet state but will show little tendency to resist distortion while in the dry state. Thus, fabrics having good wet configurational memory, i.e., spin flat drying properties, but little dry configurational memory, can be obtained essentially wrinkle-free when washed in an automatic washer and line dried but will wrinkle severely in a tumble dryer or when stored or worn. On the other hand, if cellulosic fabric also has good dry configurational memory, the fabric can be obtained substantially wrinkle-free after being dried in a tumble dryer and will resist wrinkling or mussing while stored or while being worn. This is more commonly referred to as dry crease resistance or dry crease recovery. In this respect, it is interesting to note that dry crease resistance and dry crease recovery are not necessarily synonomous. In other words, a fabric having good dry crease resistance but poorer dry crease recovery will resist low energy wrinkling or creasing but will not recover well from a crease once one has been imparted to the fabric. Such a characteristic in a fabric manifests itself by the fact that the fabric will receive a relatively high flat drying rating by A.A.T.C.C. Test Designation 88-1958 but will display a relatively low crease recovery angle according to ASTM Designation D1295-53T. Fabrics cross-linked according to the present process tend to display this phenomena. In

other words, when the fabric is subject to low energy mussing in a tumble dryer, it will display satisfactory resistance to wrinkling but when a crease is deliberately introduced as by the dry crease recovery test, the fabric may have a relatively low rating, e.g., 200°-250° (Warp + Filling) whereas conventionally resin-treated fabrics having about the same tumble flat dry rating will have somewhat higher dry crease recovery angles.

Cellulosic materials produced according to the process of this invention are characterized by cross-links of the formula

$$\text{Cel-O-CH}_2\text{-}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{-CH}_2\text{-O-Cel}$$

wherein Cel is the cellulose molecule, attached to the cross-linking bridge by the oxygen atom of one of its initially free hydroxy groups. Unmodified cellulosic materials, e.g., cotton and viscose rayon, which have not been esterified, etherified or otherwise chemically modified, will be substantially free from other forms of synthetic cross links. The cellulosic material will be substantially free from nitrogen, phosphorous, sulfur, halogen and other hetero atoms chemically bound to the cellulose molecules or the methylene or substituted methylene linkages characteristic of formaldehyde or other mono aldehyde or dialdehyde modified cotton or viscose rayon. The cellulosic material will have substantial dry and wet configurational memory. In fabrics, the material will rate above 3.0 in both the standard spin and tumble flat dry ratings, and ordinarily will rate above 4.0 in both of these tests. The dry crease recovery angle of fabrics will be above 200° and ordinarily above 220° and the wet crease recovery angle will be above 230° and ordinarily above 250°.

In carrying out the process of this invention, the selected cross-linking agent is applied to the selected cellulosic material under conditions whereby the cross-linking reaction takes place while the cellulosic material contains from 1 to 15% by weight total moisture and from 0.25% to (4R+2)% by weight strong base, calculated as NaOH, wherein R is the number of hydroxyl groups of the NaOH consumed by the selected cross-linking agent during the cross-linking reaction and the cellulosic material is in the configuration desired in the cross-linked product.

It is possible to provide emulsions of the selected cross-linking agent, strong base and water so that the appropriate amounts of moisture, strong base, and cross-linking agent are applied simultaneously to the cellulosic material. However, such emulsions are stable for only a short period of time and it is thus ordinarily preferred to apply the cross-linking agent separately from the water and strong base or at least separately from the strong base, e.g., before or after the strong base and or water. For example, the cellulosic material can be impregnated with the cross-linking agent and the appropriate amount of moisture and base then applied or an aqueous solution of the strong base applied in the correct proportions and the selected cross-linking agent thereafter applied to the cellulosic material. However, because the amount of total moisture which is to be present in the cellulosic material during the cross-linking reaction is very low, it is difficult to apply such low amounts of moisture and the strong base uniformly on the cellulosic material. For example, the moisture can be applied in the form of steam or fine mist and the selected base applied in the form of a solution or suspension in an inert organic solvent. A preferred procedure involves first uniformly distributing the strong base as an aqueous solution so that considerable more than 15% total moisture, e.g., 30%-130%, is applied to the cellulosic material and the cellulosic material then dried to the correct moisture content before the cross-linking agent is applied, as will be discussed more fully hereinafter.

The optimum amount of total moisture within the 1% to 15% range which should be present in the cellulosic material during the cross-linking reaction will depend in part, on the amount of strong base employed. It has been found that although bone dry cellulosic material is cross-linked very inefficiently with strong base and epichlorohydrin, if between 1% and 15% total moisture is present, the cross-linking reaction proceeds much more rapidly and efficiently than where larger amounts of total moisture are present. Thus, whereas about 3-5% NaOH, calculated on the weight of the dry cellulosic material is ordinarily required to achieve an efficient cross-linking reaction when the moisture content of the cellulosic material is, e.g., 35% or more, the cross-linking efficiency of the strong base catalyst increases rapidly as the total moisture content of the cellulosic material drops below 15% so that as little as 0.25% NaOH, e.g., 0.5%-3%, is required. Optimum reaction rates exist when the total moisture content of the cellulosic material is between 3% and 12% by weight and greatest dry configurational memory is imparted to the cellulosic material in this moisture range. Preferably the ratio of water in percent to strong base in percent calculated as NaOH, based on the weight of the cellulosic material, is 1:1 to 10:1, more preferably 2:1 to 5:1.

Good results are obtained with cotton fabric by padding the fabric with 1% to 4% by weight aqueous NaOH, squeezing the fabric to provide a pick up of the solution of 30%-130%, e.g., 50%-100%, calculated on the weight of the starting dry

fabric so as to provide between 0.5% and 6%NaOH on the fabric, drying the fabric, e.g., over dry cans or in a curing oven with tenter frame, preferably so that the fabric temperature does not exceed 100°C. and more preferably does not exceed 90°C., to a total moisture content between 1% and 15%, thus providing fabric uniformly impregnated with the correct amount of moisture and strong base, and thereafter applying e.g., by means of an applicator roll, the selected amount of epichlorohydrin or compound which is converted to epichlorohydrin in the presence of strong base. The amount of epichlorohydrin which is applied is preferably in molar excess of the amount of strong base present in the fabric and is preferably in the range of 2%-15%, e.g., 4%-12%, calculated on the weight of the dried fabric. If dichloropropanol is employed as cross-linking agent, it is desirable to employ slightly less than 0.5 molar equivalent so as to obtain a still alkaline fabric at the end of the cross-linking reaction. If more than a 0.5 molar amount of dichloropropanol is employed, insufficient cross-linking may result. For these reasons epichlorohydrin is the preferred cross-linking agent. If the fabric is rolled up in a smooth roll during the cross-linking reaction, the epichlorohydrin vapours will diffuse between the layers, thereby ensuring uniform cross-linking, even though the epichlorohydrin is not applied exactly uniformly.

As stated above, the cellulosic material has uniformly distributed therein the strong base and moisture during the cross-linking reaction. The term "uniformly" as used herein means that relatively large areas, e.g., one square inch, of cellulosic material will have substantially the same moisture and base content as other relatively large areas. On the other hand, irregularities in the moisture and strong base content in very small areas, e.g., 0.05 square inch or less, are not precluded so long as the overall effect is one of uniformity.

The selected cellulosic material containing the strong base, moisture and selected cross-linking agent is then maintained at a temperature up to 100°C., preferably between room temperature and 60°C., until the desired cross-linking reaction has taken place. These temperatures refer to the environmental temperature in which the cellulosic material is maintained. The actual temperature of the cellulosic material may exceed these temperature ranges, due to the exothermic nature of the reaction. Ordinarily. it is preferred that the environmental temperature is at least 25°C. so that the cross-linking reaction will proceed at a reasonable rate. When the environmental temperature in which the cellulosic material is maintained is between 60°C. and 100°C., the reaction is substantially complete in a few seconds to a few minutes. However, it is ordinarily preferred to conduct the reaction while the cellulosic material is in an environmental temperature of between 20°C. and 60°C. and with these conditions, particularly if the cellulosic material is in a compacted state, the reaction is substantially complete in less than 6 hours.

The cross linked cellulosic material is then ordinarily washed thoroughly to remove any last traces of reactants and finished in the usual manner, e.g., by drying in a tenter frame. When the preferred reactants and reaction conditions are employed, the resulting cellulosic material thus obtained will have outstanding dry and wet configurational memory. For example, cotton fabric of the broadcloth or printcloth type will often retain about 50% or more of its bleached and mercerized strength and will rate 4.0 or better by the standard flat drying test after being spin and line dried or spin and tumble dried.

The following examples are illustrative of the products and processes of this invention but are not to be construed as limiting. The percentage compositions referred to in the Examples are by weight.

EXAMPLE I

Cotton sheeting containing the usual 6-7% moisture is uniformly padded with 15% NaOH in a 50:50 mixture of methanol and water to obtain a 55% pick-up thereof, thus providing 8.3% NaOH, calculated on the weight of the starting fabric or 8.8%, calculated on the bone dry fabric. The wet fabric is dried until 84% of the applied solution has volatilized, thus providing fabric containing 6% total moisture and 7.7% NaOH, calculated on the total weight of the dried fabric. 25% dichloropropanol (90% purity) in methanol is then applied by means of an applicator roll with a 59% pick-up, calculated on the weight of the dried fabric. The fabric is maintained in a polyethylene encased smooth roll in an oven at 55°C. for 16 hours and then washed thoroughly and tested. The fabric thus treated will have about 34 lbs. residual filling tensile strength and will receive about a 4.2 spin dry and a 4.7 tumble dry flat dry rating.

EXAMPLE II

Cotton sheeting conditioned to 6% moisture content is uniformly impregnated with 15% aqueous NaOH containing 0.5% dispersed starch at a 58% pick-up. The fabric is then dried to volatilize 80% of the caustic solution. The dried fabric thus contains 8% total moisture, 8% NaOH and 0.3% starch.
0.3% starch.
calculated on the total weight of the dried fabric.

To the dried fabric is applied, by an applicator roll, a 50:50 mixture of dichloro-

propanol (90% purity) and methanol with a 39% up-take. The fabric is then heated at 55°C. for 20 hours in a polyethylene encased smooth roll, washed thoroughly and tested. Fabric thus treated will have about a 4.0 spin dry and a 3.7 tumble dry flat dry rating.

EXAMPLE III

Cotton sheeting containing 6% moisture is uniformly impregnated with 10% aqueous NaOH with a 68% pick-up. The fabric is dried to a weight gain of 14.4% calculated on the starting fabric. The fabric thus contains 13% total moisture and 6% NaOH, calculated on the total weight of the dried fabric.

16% calculated on the weight of the dried fabric of epichlorohydrin is applied by means of an applicator roll on the dried fabric which is then maintained in a polyethylene encased smooth roll for 16 hours at 55°C. and then washed and tested. Fabric thus treated will receive about a 4.6 spin dry and 4.0 tumble dry flat dry ratings.

EXAMPLE IV

The procedure of Example III is followed, employing 7.5% aqueous NaOH with a 70% pick-up and drying to a ewight gain of 17%, calculated on the starting fabric to provide 15% total moisture and 4.5% NaOH, calculated on the total weight of the dried fabric. 8% calculated on the weight of the dried fabric of epichlorohydrin is applied by means of an applicator roll to the dried fabric which is then aged in a polyethylene encased smooth roll for 16 hours at 55°C. washed and tested. Fabric thus treated will receive about a 4.8 spin dry and a 3.0 tumble dry flat dry rating.

EXAMPLE V

The procedure of Example III is followed with a 69% pick-up of 7.5% NaOH and a residual weight gain of 13% after drying, thus providing fabric containing 12% total moisture and 4.5% NaOH, calculated on the total weight of the dried fabric. 3% calculated on the weight of the dried fabric of epichlorohydrin is applied and the fabric aged as described in Example III. Fabric thus obtained will receive about a 5.0 spin and a 3.8 tumble flat dry rating.

EXAMPLE VI

The procedure of Example V is followed with about a 65% pick-up of 5% NaOH and drying to give a negligible weight gain after drying, thus providing fabric containing 3% NaOH and 3% total moisture, calculated on the total weight of the dried fabric. Substantially the same amount of epichlorohydrin is picked up. The treated fabric will obtain about a 4.8 spin dry and 3.3 tumble dry flat dry rating.

EXAMPLE VII

80 × 80 standard cotton printcloth is uniformly padded with a 5% aqueous solution of NaOH with an 80% pick-up thereof. The fabric is then dried to about 10% total moisture over dry cans heated with steam at about 17 lbs. pressure, thus providing fabric having uniformly distributed therein 10% total moisture and 3.8% NaOH, calculated on the total weight of the fabric. There is uniformly applied 15% epichlorohydrin to the dry fabric to provide a large molar excess thereof, calculated on the NaOH. The fabric is aged overnight at 55°C. in a polyethylene encased smooth roll and then washed and tested. The fabric will receive about a 5.0 spin and 4.8 tumble flat dry rating.

Substituting 6% NaOH for the 5% NaOH, thus providing about 4.5% NaOH, calculated on the total weight of the dried fabric, produces fabric having substantially the same spin and tumble flat dry ratings.

EXAMPLE VIII

The procedure of Example VII is followed except that the starting fabric contains 6% polyethylene softener (Moropol 700) uniformly dispersed therein. Fabric treated with 5% aqueous NaOH and dried will receive about a 5.0 spin and 4.5 tumble flat dry ratings.

Fabric similarly treated with 4% or 6% aqueous NaOH will also receive about the same spin and tumble flat dry ratings.

EXAMPLE IX

136 × 64 cotton broadcloth is uniformly impregnated with 4.5% aqueous NaOH with a 70% pick-up. The fabric is dried open width on tenter frame to 3% total moisture, thus providing fabric containing 3% NaOH, both calculated on the total weight of the dried fabric. To the dried fabric is evenly applied 8-12% epichlorohydrin and the fabric is then maintained at 35°C. overnight in a polyethylene encased smooth roll, washed, top softened with polyethylene softener, and tested. The fabric will receive about a 4.7 spin and 5.0 tumble flat dry ratings.

Fabric dried to 5% total moisture will receive about the same flat dry ratings. Fabric dried to 10% total moisture will rate about 4.9 × 4.7 and fabric dried to 15% total moisture will rate about 5.0 × 3.7.

EXAMPLE X

The procedure of Example IX is followed with 180 count cotton percale sheeting. Fabric dried to 5% total moisture will rate about 4.1 × 4.5. Fabric dried to 10% total moisture will rate about 4.3 × 4.2 and fabric dried to 15% total moisture will rate about 4.6 × 3.4.

WHAT WE CLAIM IS:—

1. A process for imparting improved wet and dry configurational memory to cellulosic material comprising cross-linking free hydroxy groups of the cellulosic material with a cross-linking agent comprising epichlorohydrin or a compound

which is converted to epichlorohydrin in the presence of a strong base as herein defined, the cross-linking reaction being conducted while the cellulosic material has uniformly distributed therein, calculated on the total weight of the cellulosic material, from 1% to 15% total moisture and from 0.25% to (4R+2)% strong base, calculated as NaOH, wherein R is the number of hydroxyl groups of the NaOH consumed by the cross-linking agent during the cross-linking reaction, and the cellulosic material containing moisture, strong base and cross-linking agent being maintained in the desired configuration at a temperature up to 100°C. until the desired cross-linking reaction has taken place.

2. A process according to claim 1, wherein the cross-linking agent is dichloropropanol.

3. A process according to claims 1 or claim 2, wherein the cellulosic material is cotton.

4. A process according to any of claims 1-3, wherein the cellulosic material is cotton fabric.

5. A process according to claim 4, wherein the fabric is maintained in a smooth condition during the cross-linking reaction.

6. A process according to claim 5, wherein the fabric is maintained in roll form.

7. A process according to any of the preceding claims, wherein the cross-linking reaction is conducted at from room temperature to 60°C.

8. A process according to any of the preceding claims, wherein the strong base is an alkali metal hydroxide.

9. A process according to any of the preceding claims, wherein the strong base is sodium hydroxide.

10. A process according to claim 1, wherein the cross-linking agent is epichlorohydrin and the strong base is sodium hydroxide, a molar excess of the epichlorohydrin, calculated on the sodium hydroxide, being applied to the material.

11. A process according to any of claims 8-10, wherein the amount of the hydroxide is between 0.5% and 4%.

12. A process according to any of the preceding claims, wherein the total moisture content is between 3% and 12%.

13. A process according to any of the preceding claims, wherein the cross-linking agent is applied to the cellulosic material after the material has uniformly distributed therein the moisture and the strong base.

14. A process according to claim 13, wherein an aqueous solution of the strong base is applied to the cellulosic material in an amount sufficient to provide, calculated on the weight of the starting material, from 30% to 130% of the total moisture, and the cellulosic material is then dried to a total moisture content between 1% and 15%.

15. A process according to claim 13, wherein the aqueous solution of the strong base is a 1-4% solution of an alkali metal hydroxide which is applied to the cellulosic material is an amount sufficient to provide a pick up of the solution of from 30-130%, calculated on the weight of the starting material, so as to distribute on the material between 0.5-6% alkali metal hydroxide.

16. A process according to claim 14 or claim 15, wherein the material is dried at a temperature below 90°C.

17. A process according to claim 1 for imparting improved wet and dry configuration memory to cellulosic material substantially as hereinbefore described with particular reference to the Examples.

18. Cellulosic material having improved wet and dry configurational memory when produced by a process according to any of the preceding claims.

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